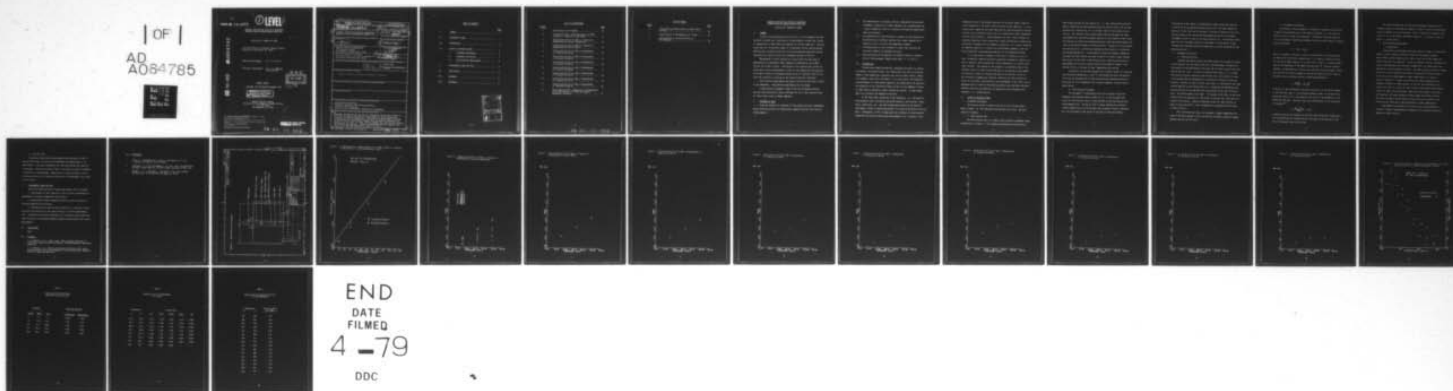AD-A064 785   GENERAL ELECTRIC CO PHILADELPHIA PA RE-ENTRY AND ENV--ETC F/G 11/4
CHEMICAL AND PHYSICAL ASPECTS OF MESOPHASE FORMATION DURING CAR--ETC(U)
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CHEMICAL AND PHYSICAL ASPECTS OF MESOPHASE
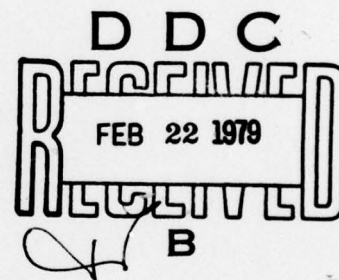FORMATION DURING CARBON-CARBON PROCESSING

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Contract No. F49620-78-C-0006

Air Force Office of Scientific Research (AFSC)
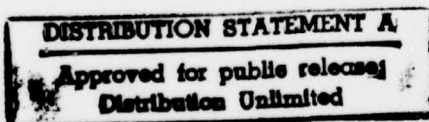Bolling Air Force Base, DC   20332

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coal tar pitch, phenanthrene, anthracene, acenaphthene

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Equipment designed around the use of a laboratory Instron test machine is described for making high pressure measurements of sound velocity and viscosity at elevated temperature. Sound velocity measurements were made in phenanthrene at temperatures between 393K and 562K and pressures between 0.1 and 101 MPa. A linear relation between the cube of sound velocity and pressure was observed. Velocity measurements were also made in coal tar pitch in the same temperature range at 0.1 MPa.

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CHEMICAL AND PHYSICAL ASPECTS OF MESOPHASE
FORMATION DURING CARBON-CARBON PROCESSING

Contract No. F49620-78-C-0006

I.   SUMMARY

A small scale high pressure cavity (5 cm x 1.27 cm diameter) has been modified to enable sonic velocities to be determined in various test liquids at temperatures to about 700°C and pressures to 101 MPa (1000 bar). Pressure within the cell is applied by means of a laboratory Instron testing machine. Modifications include air-free cell filling and specimen extraction set-ups, transducer and timing circuitry and isothermal heating of the cell.

Measurements of sonic velocity at 2 and 6.5 MHz have been made in phenanthrene (a polyaromatic model compound) at temperatures up to 690K (317°C) and 101 MPa (1 Kbar). Calibration of cell pressure was carried out using sonic velocity measurements in water at room temperature and pressures to 101 MPa (1 Kbar); an estimated pressure error of 3 percent exists at this level due primarily to friction at the pressure seal/cell interfaces.

Sonic velocity measurements were made in Allied 277-15V pitch to 270°C at one atmosphere. High pressure measurements are in progress.

A high pressure viscometer, based on the falling needle principal has been constructed and is being calibrated for use in the viscosity range of liquid pitch as well as model compounds.

II.   STATEMENT OF WORK

1.   Study the chemistry of formation of the graphite precursor (mesophase) during pressure pyrolysis of carbon-carbon composite matrices with the following emphasis:

1.1   The determination of viscosity, density, compressibility and other fundamental properties of a model compound such as phenanthrene and a typical commercial pitch as a function of processing temperatures, times and pressures.

1.2   The determination of the influence of pressure on the formation and characteristics of mesophase derived from a model compound and a commercial pitch in various time-temperature regimes.

1.3   The determination of the influence of carbon fiber surfaces and structural chemistry on mesophase formation.

1.4   Characterization of the physical and chemical aspects of graphitization of the mesophase formed during tasks 1.1, 1.2 and 1.3.

III.   INTRODUCTION

Carbon-carbon composite materials, developed originally for nosetip and thermal shield applications, are finding their way into an increasing number of high temperature structural uses such as rocket nozzles, combustion chambers, brake discs and others. To a large extent, the properties and performance of carbon-carbon composites are determined by the selection and properties of the reinforcing fibers as well as such geometric factors as fiber bundle orientation, angle, packing and spacing. To some degree, these are calculable and amenable to analysis.

On the other hand, processing of the composites, i.e., the materials and parameters used in achieving the desired density, load transfer, fiber/matrix interaction, etc., has been accomplished essentially by empirical development, aiming at optimum performance in an erosive and ablative environment. Consequently, little is known about the influence of source material properties and variation and processing parameters (e.g., pyrolysis, time-

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temperature cycle of the organic precursor of the matrix phase, pressure) on the properties of the matrix itself or those of the composite. To date, carbon-carbon composites have been densified by repetitive pyrolysis/graphitization cycles applied to liquid coal tar or petroleum pitches impregnated into the fibrous preform. These procedures and their varied influence on composite properties, matrix properties, process optimization, productivity and capital investment are not amenable to analysis. As a result, modeling of composite behavior as a function of reinforcement geometry, fiber and matrix properties and processing conditions is not presently possible.

To a large extent, progress in this area is limited by a lack of basic information regarding precursor properties and behavior, physical as well as chemical, during processing, either separately or in contact with fiber surfaces. The purpose of this program is to determine some of the essential values of liquid pitch properties in the processing environment. In particular, values of viscosity and density are desired, as well as the influence of temperature, pressure, additives and fiber surface condition on the origin, characteristics and development of the liquid crystal mesophase which is known to form during pysolysis and from which the matrix graphite structure and properties are generated during subsequent heat treatment, i.e., graphitization.

IV.   STATUS OF RESEARCH EFFORT

1. Equipment Development

The research effort is based on the use of two principal experimental systems - a) the laboratory high pressure cell and b) the high pressure viscometer.

a. High Pressure Cell

The high pressure cell is a simple piston cylinder arrangement shown schematically in Figure 1. This system was designed and constructed on

IRAD funding during 1977 and consists of: i) two, thick-walled cylinders made of Udimet-700 and 304 stainless steel for high (to 700°C) and low temperature use, respectively; ii) an Inconel liner for the working cavity; and iii) two stainless steel pistons which comprise the upper and lower containment walls and which transmit pressure to the contents of the cavity. The pistons are fitted with compressible metal rings that deform against the liner of the working chamber to effect the seal. Pressure on a fluid within the working cavity is achieved by compressing the pistons in a laboratory Instron testing machine. A piezoelectric crystal and detector mounted on the upper and lower pistons are used to send an ultrasonic signal through the pistons and the fluid in the working cavity, enabling sound velocity measurements to be used to monitor physical and chemical changes in the working fluid as a function of time, temperature and pressure.

Accessories for the high pressure cell include a heater for achieving and maintaining temperature, a cell filling system with which the working cavity can be evacuated and filled with the molten experimental material kept under an inert atmosphere, and a piston alignment, insertion and removal device.

b. High Pressure Viscometer

The viscometer is constructed from a 30 cm length of Autoclave Engineers high pressure tubing, 0.4865 cm I.D. A ferrite needle comprises the falling body, and is raised and held at the starting position electromagnetically. During its fall it passes through two ultrasonic signals beamed across the fluid within the viscometer channel, separated by a 10 cm distance in the center of the tube to avoid end effects.

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Interruption of the signal is electronically timed so that the viscosity of the fluid can be measured from the time of fall, the path length and densities of the fluid and falling body. Pressure is applied to the fluid column by means of the Instron testing machine acting on a piston-seal arrangement similar to that of the high pressure cell. The accessory equipment for this instrument consists of the heater, filling device, piston alignment and withdrawal device and electronic circuitry described for the high pressure cell.

2. Equipment Calibration

a. High Pressure Cell

Although the pressure within the high pressure cell system as a whole can be computed from the Instron load cell, the measurement includes pressure applied to the experimental fluid plus the frictional drag of the seals against the cell liner. In order to calibrate the system, i.e., to determine pressure actually applied to the working fluid, the velocity of sound in de-ionized water was determined as a function of pressure at room temperature. Results are given in Table I and Figure 2. Measurements were made at both approach to and retreat from (i.e., increasing and decreasing) the pressure setting to evaluate the error associated with the seal frictional drag. The effect appears to be small. For example at 90.2 MPa (13,100 psig) sound velocity was measured as 1.649 km/sec on approach and 1.653 km/sec on retreat from pressure. Based on literature values for sound velocity in water at high pressure[1], this corresponds to a pressure error of about 1.2 MPa (178 psi).

This calibration may have to be repeated at higher temperatures because of possible changes in seal friction due to thermal expansion changes between the seal and cell wall.

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b. Viscometer Calibration

Calibration of the viscometer is currently in progress using liquids of known viscosity which are in the range of interest, i.e., near the viscosity of coal tar pitch (0.1-100 poise). Calibration involves selection of a falling body of appropriate diameter for the viscosity range of interest, using the relation:

$$\eta = C(\rho_n - \alpha\rho_e)t$$

where η is dynamic viscosity, ρ_n and ρ_e are densities of the falling body or needle and of the fluid, respectively, α is a density correction factor for the liquid under pressure, t is time of fall, and C is a constant depending on the dimensions of the needle and capillary.[2] The most suitable diameter, corresponding to a more or less specified viscosity range, limited by correction for kinetic energy on one hand and unduly long fall times on the other, can be obtained from the following approximation:

$$C = \frac{g R^2 Z}{6L} \left(\frac{1 - Z}{1 + Z}\right)^3$$

in which g is the acceleration constant of gravity, R is the inner diameter of the capillary tube, L is the distance between centers of the monitoring ultrasonic beams and Z is the square of the ratios of the diameters of the needle and the tube. There are other such relationships in the literature, for example:[3]

$$K = \frac{(D_2 - D_1)g}{24D_2} \cos \emptyset$$

in which D_2 and D_1 are diameters of the tube and falling body, respectively, g is the gravitational constant and $\emptyset$ is the angle to the vertical of the fall of the needle, zero in this case.

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All such relations must be used with experimental determination of
a known viscosity in the range of interest in order to derive an appropriate
value of diameter of the falling body. This is currently in progress using
castor oil (η = 9.86 poise), and benzyl alcohol (η = 5.8 poise) as well as
water (η = 0.0103 poise).

3. Sound Velocity Measurements

a. Phenanthrene

Sound velocity measurements have been made at 6.5 MHz in liquid phenan-
threne, a model compound selected for baseline measurements between,
394K (120°C) and 562K (289°C) and 0.1 MPa (1 atm) and 101 MPa (1000 atm).
Table 2 shows the data obtained. As was anticipated, velocity increases with
pressure and decreases with increasing temperature, the former effect pre-
dominating as both parameters increase. The cube of sound velocity in liquids
should be a linear function with respect to pressure[3] and this appears
to be the case for phenanthrene at lower temperatures as is seen by
Figures 3 through 11. Breaks in the curves at higher temperatures are
probably indicative of lower pressure in the cell than indicated by the
Instron cell load as a result of seal friction, particularly where velocity
values are lower than anticipated. Where velocities appear to be higher
than expected, one might postulate a phase change from liquid to solid.
This does not appear likely because of the similarity in slopes of the
curves and the linearity of the relationship at lower temperatures.

Measurements are planned for the near future using anthracene, a
structural isomer of phenanthrene to determine the influence of molecular
geometry on sound velocity.

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b. Coal Tar Pitch

Preliminary sound velocity measurements were obtained at 2 MHz in Allied 277-15V coal tar pitch at one atmosphere and temperatures up to 240K (268°C). High sound attenuation at 6 MHz necessitated the reduction in frequency. Results are given in Table 3 and shown in Figure 12 compared to velocities in phenanthrene, Determination of sound velocity in pitch at increased pressure is planned as the next set of measurements to be made in this series.

V.   EXPERIMENTAL PLANS FOR 1979

During the coming year the following experimental work is planned.

1. Measurement of sound velocity in coal tar pitch, anthracene and acenaphthene at elevated temperature and pressure.

2. Measurement of model compound and coal tar pitch viscosity at elevated temperature and pressure.

3. Determination of coal tar pitch stability as a function of time. using the high pressure cell and sound velocity as a kinetic measurement tool. Examination of post-test specimens will be done by optical polarized light microscopy to correlate mesophase content and description with kinetic measurements.
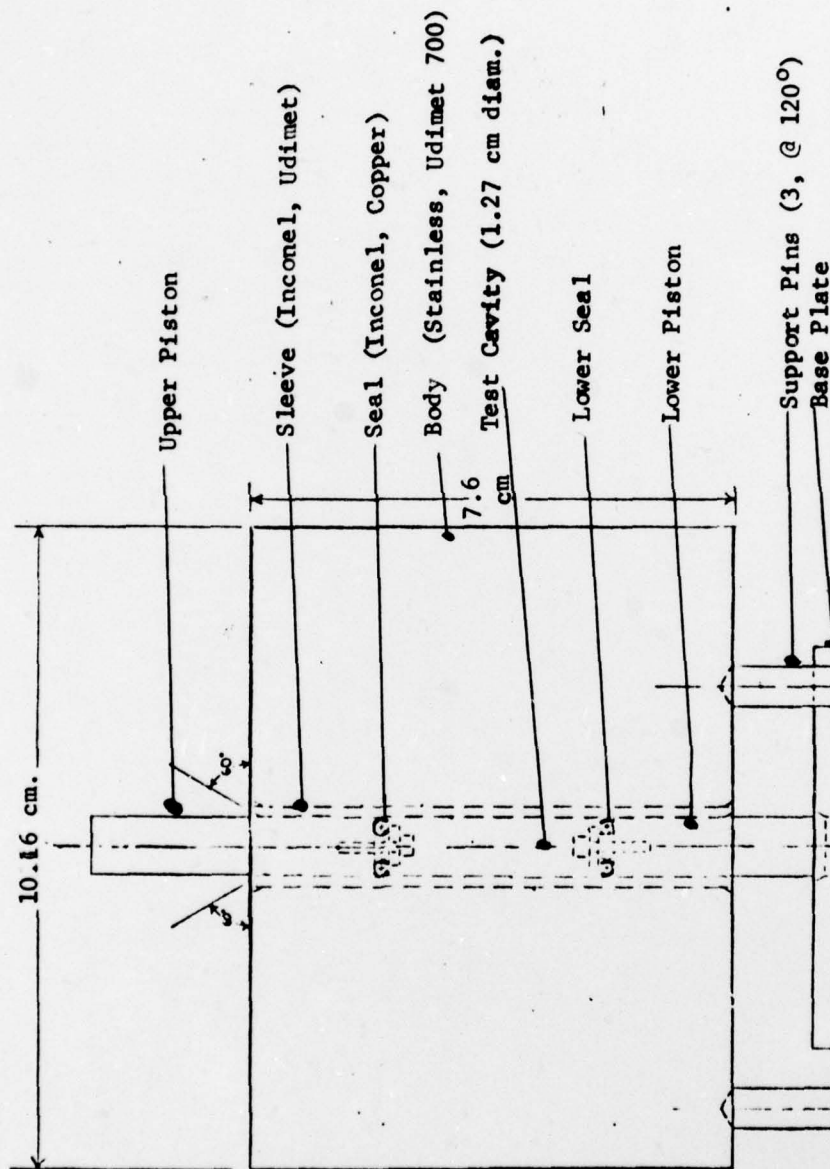
VI.   PUBLICATIONS

None

VII. PERSONNEL

J. J. Gebhardt, D. Sc., Phys. Chem., 1951, Carnegie Institute of Technology, Consulting Physical Chemist, Advanced Materials Laboratory Operation.

J. A. Roetling, B. S., Physics, University of Buffalo, 1941, Supervising Engineer, Physical and Mechanical Testing Laboratory, Advanced Materials Laboratory Operation.

VIII. REFERENCES

1. Holton, G., Hagelberg, M. P., Kao, S. and Johnson, W. H. Jr.,
    J. Acoust. Soc. $\underline{43}$ (1) 102-167 (1968).

2. Boelhouwer, J. W. M. and Toneman, L. H., Proc. Conf. on Lubrication
    and Wear, London 1959, pp. 214-218, London Institute of Mech. Eng.

3. Mamedov, I. A., Faizoolaev, Z. and Aliev, A. M., Trans. Higher
    Training Inst. of Oil and Gas, #10 $\underline{1973}$, pp. 65-68.

Figure 1 - High Pressure Cell Assembly

Upper Piston

Sleeve (Inconel, Udimet)

Seal (Inconel, Copper)

Body (Stainless, Udimet 700)

Test Cavity (1.27 cm diam.)

Lower Seal

Lower Piston

Support Pins (3, @ 120°)

Base Plate

7.6 cm

10.16 cm.

SIDE VIEW

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Figure 2. Calibration Curve - Sound Velocity at 6.5 MHz in Water vs. Pressure at 303K (30°C). Solid Line from Data in Ref. 1.
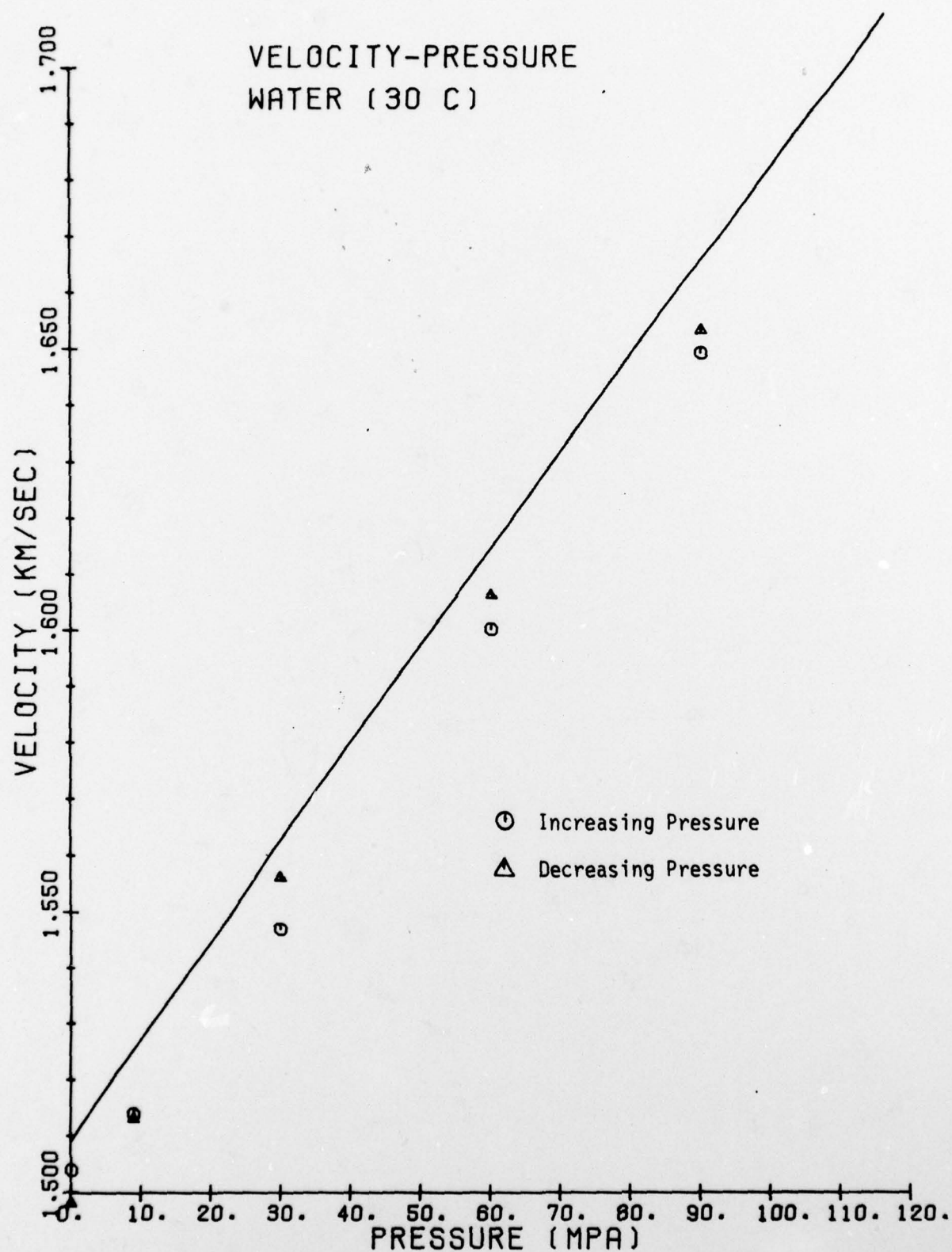

VELOCITY-PRESSURE
WATER (30 C)

○ Increasing Pressure
△ Decreasing Pressure

VELOCITY (KM/SEC)

PRESSURE (MPA)

Figure 3. (Sound Velocity)[3] at 6.5 MHz vs. Pressure in Phenanthrene at Various Temperatures.
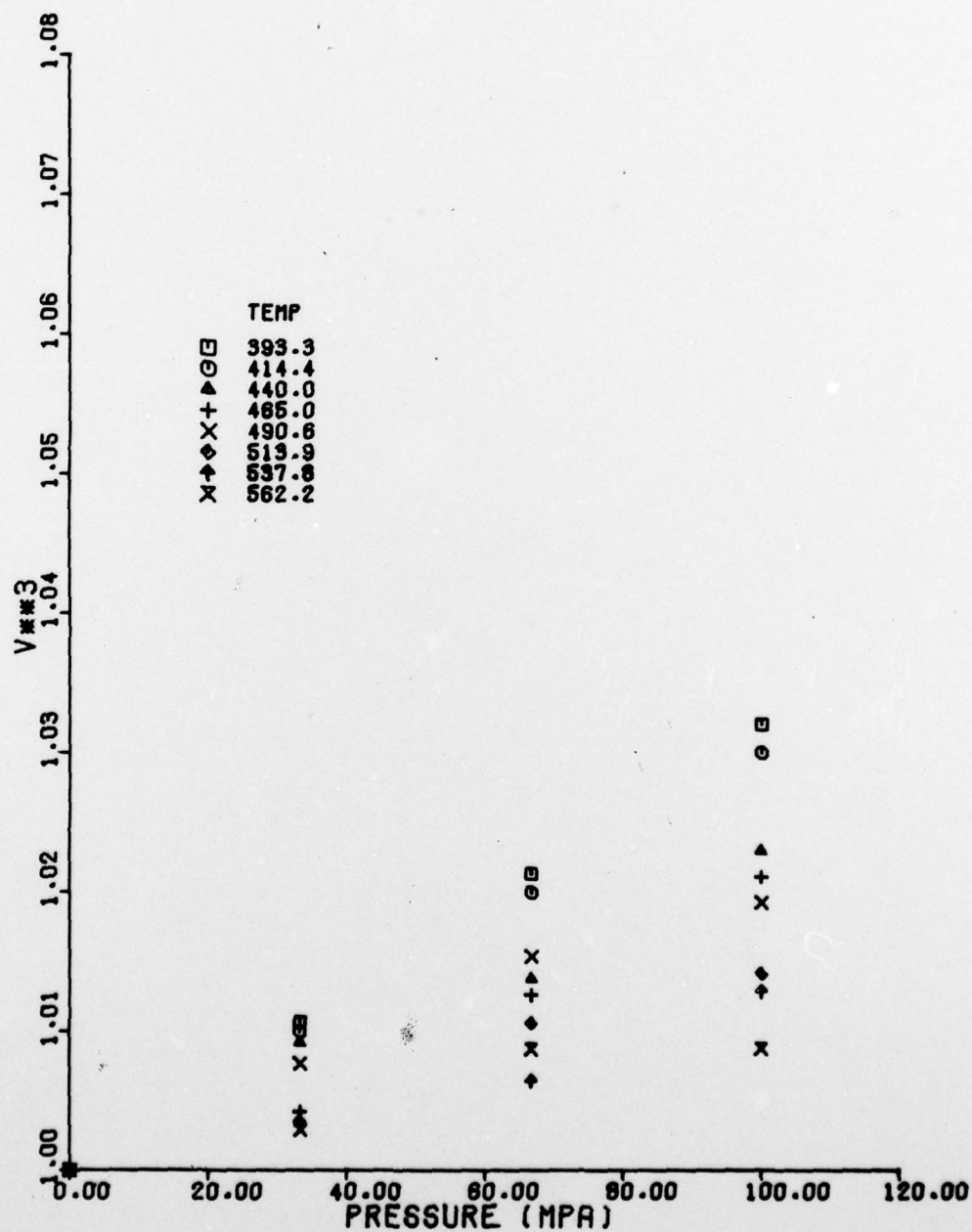
Figure 4. (Sound Velocity)^3 at 6.5 MHz vs. Pressure in
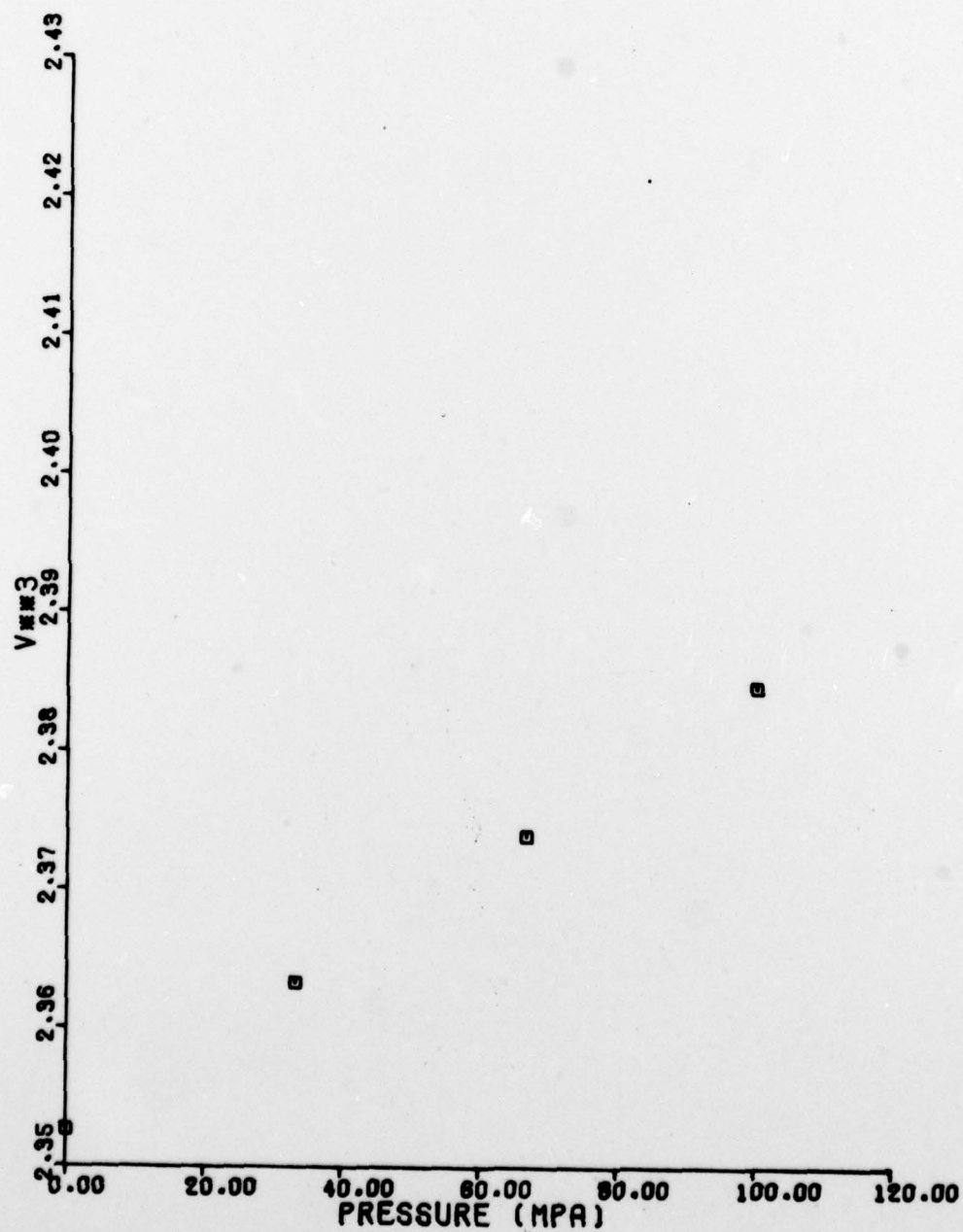Phenanthrene at 393.3K (120°C).

TEMP= 393.3

13

Figure 5. (Sound Velocity)[3] at 6.5 MHz in Phenanthrene vs. Pressure at 414.4 K.
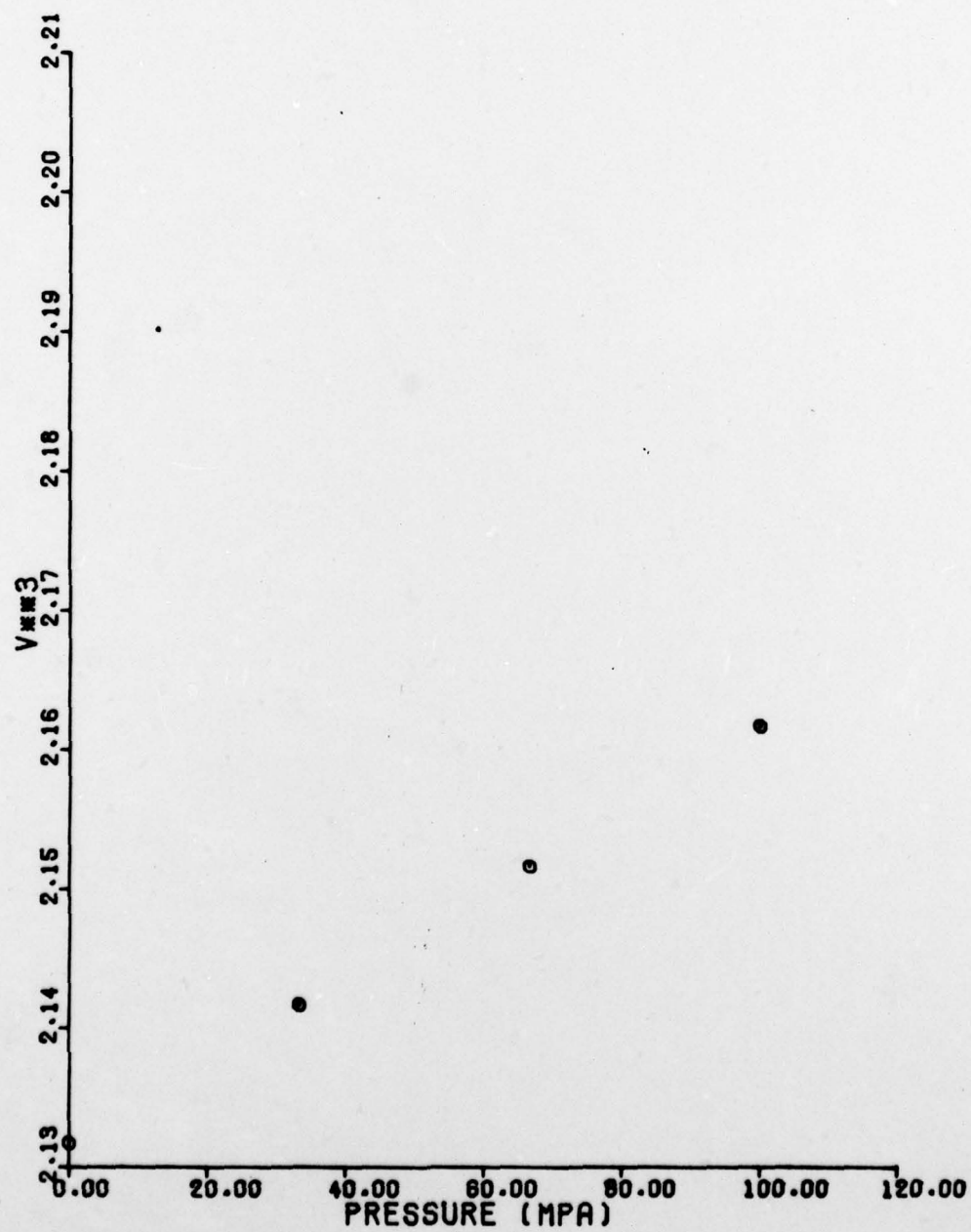
TEMP= 414.4

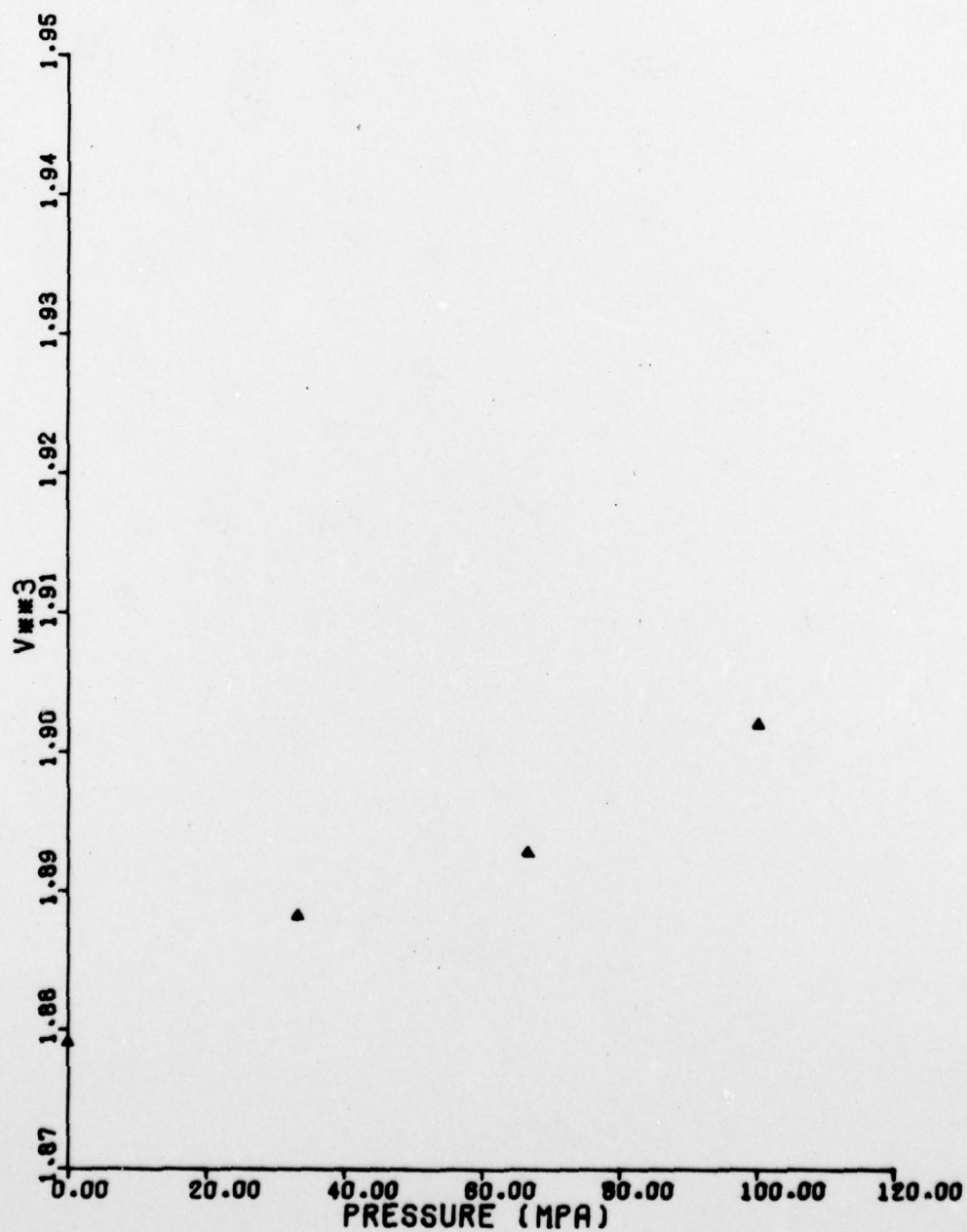Figure 6. (Sound Velocity)^3 at 6.5 MHz in Phenanthrene
vs. Pressure at 440.0K.

Figure 7. (Sound Velocity)^3 at 6.5 MHz in Phenanthrene vs. Pressure at 465.0K.

TEMP= 465.0

Vᴴᴴᴴ3

1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.65

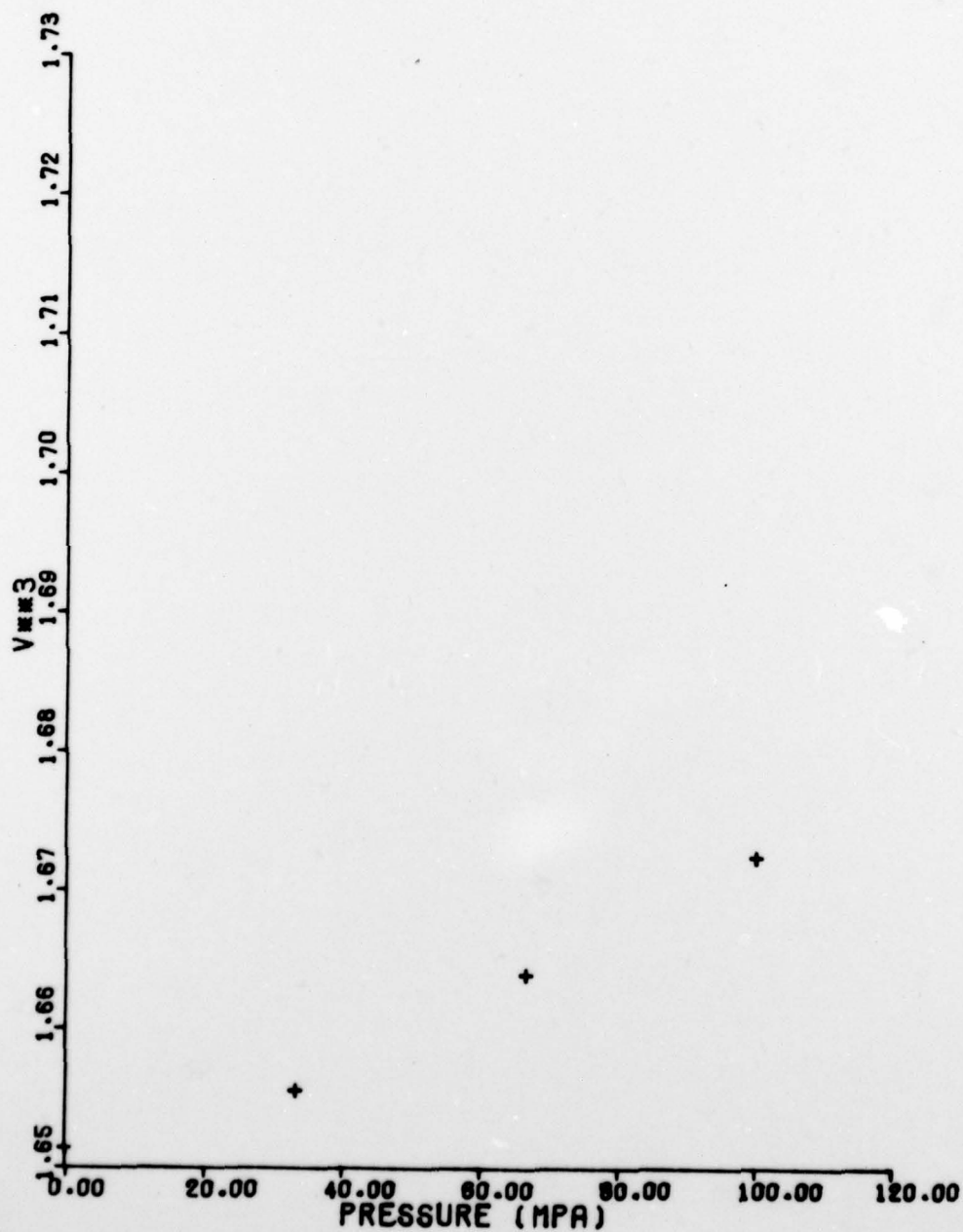0.00   20.00   40.00   60.00   80.00   100.00   120.00
PRESSURE (MPA)

16

Figure 8. (Sound Velocity)^3 at 6.5 MHz in Phenanthrene
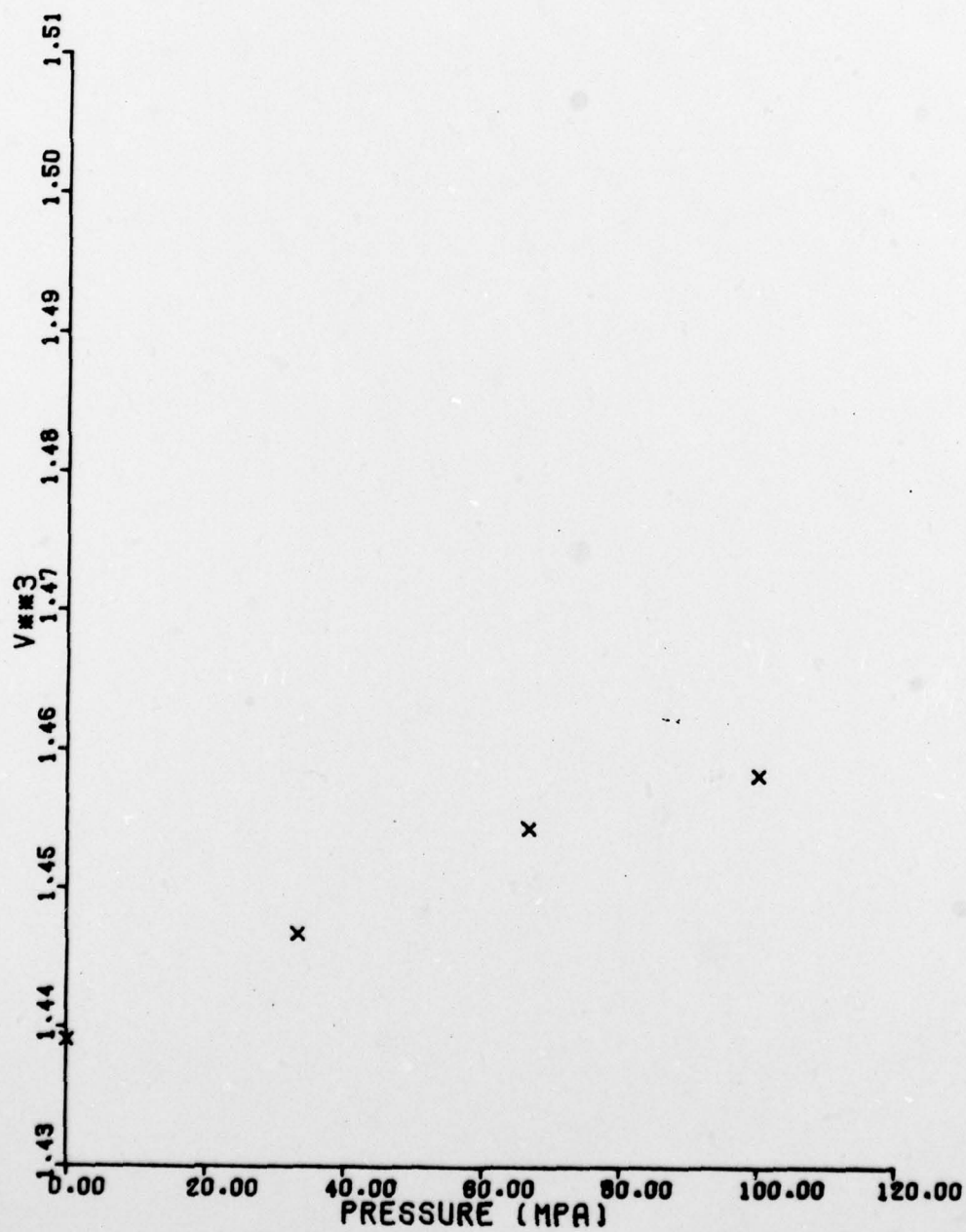vs. Pressure at 490.6K.

Figure 9. (Sound Velocity)^3 at 6.5 MHz in Phenanthrene
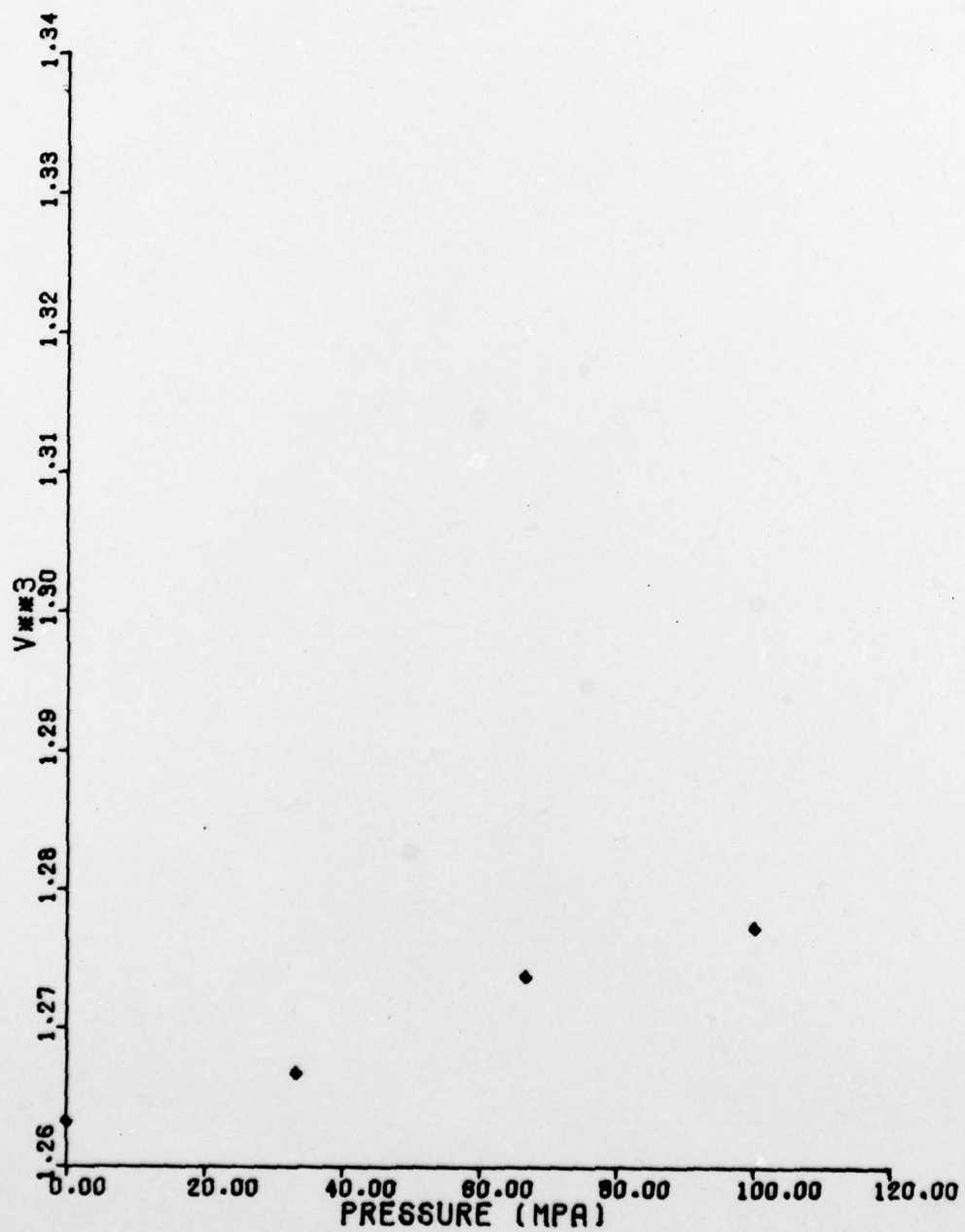vs. Pressure at 513.9K.

TEMP= 513.9

Figure 10. (Sound Velocity)^3 at 6.5 MHz in Phenanthrene vs. Pressure at 537.8K.

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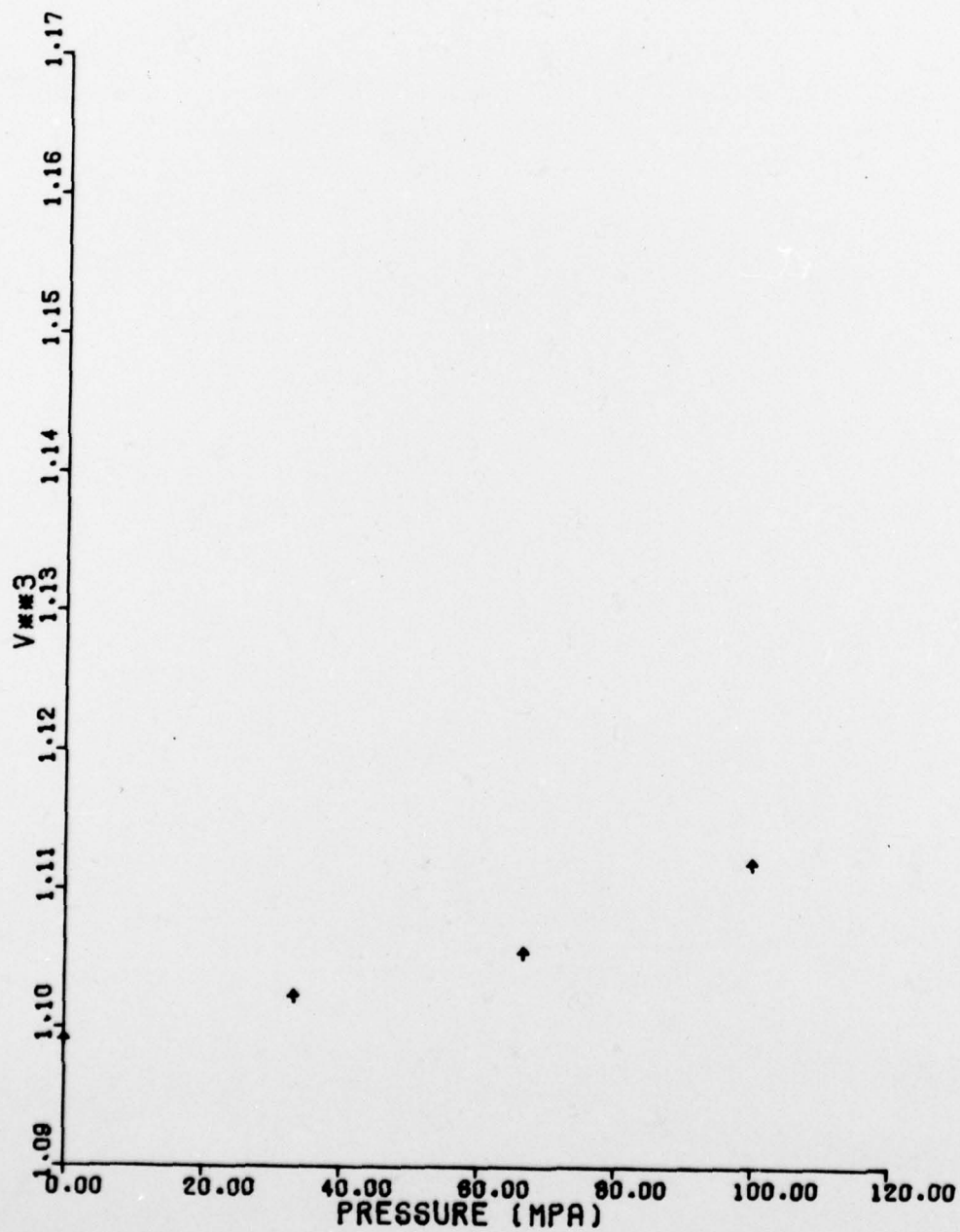Figure 11.   (Sound Velocity)[3] at 6.5 MHz in Phenanthrene
vs. Pressure at 562.2K.

TEMP= 562.2

V**3

1.02

1.01

1.00

.99

.98

.97

.96

.95

.94

0.00   20.00   40.00   60.00   80.00   100.00   120.00
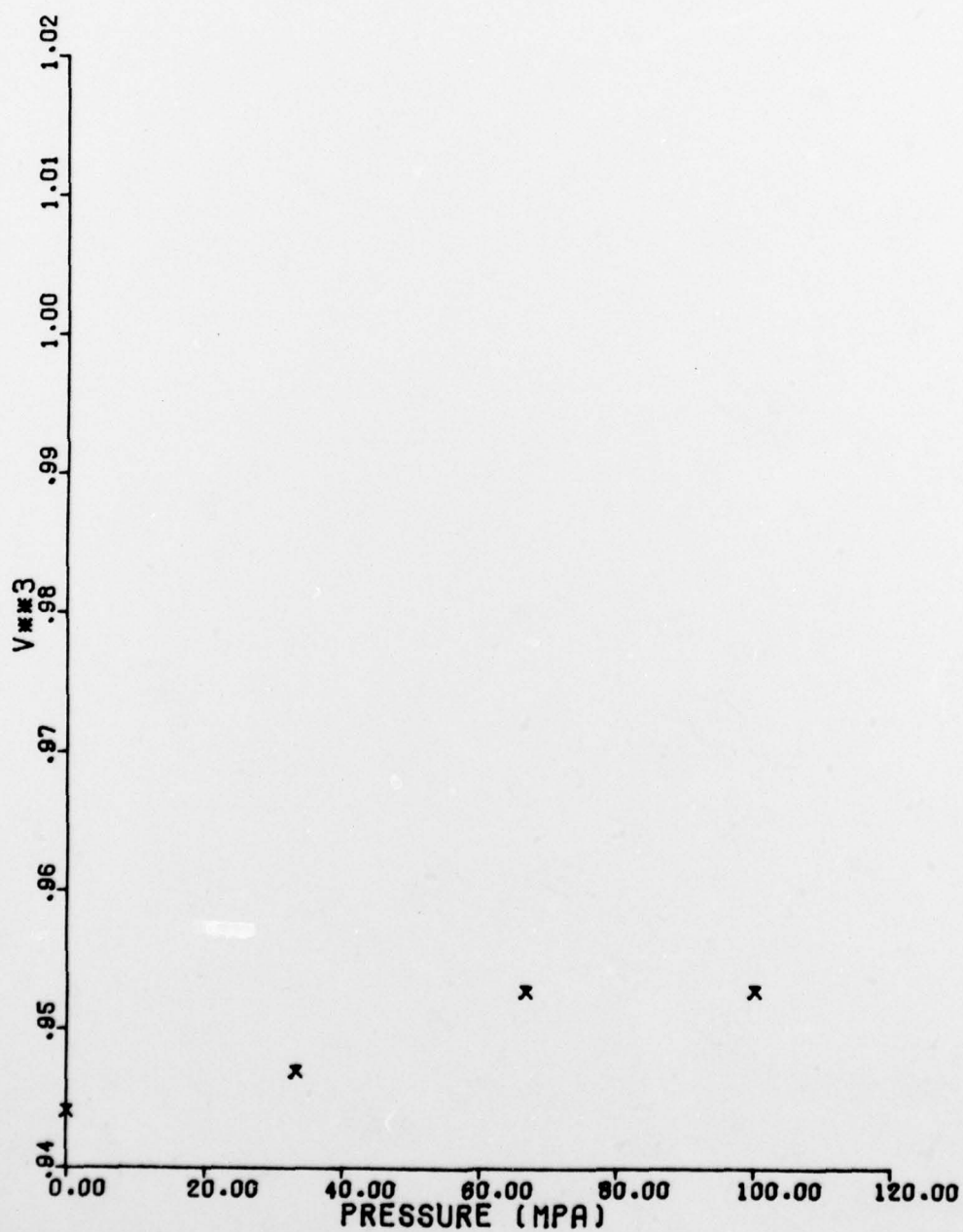PRESSURE (MPA)

20

Figure 12. (Sound Velocity)^3 vs. Temperature in Phenanthrene at 6.5 MHz and Coal Tar Pitch at 2 MHz at Atmospheric Pressure.
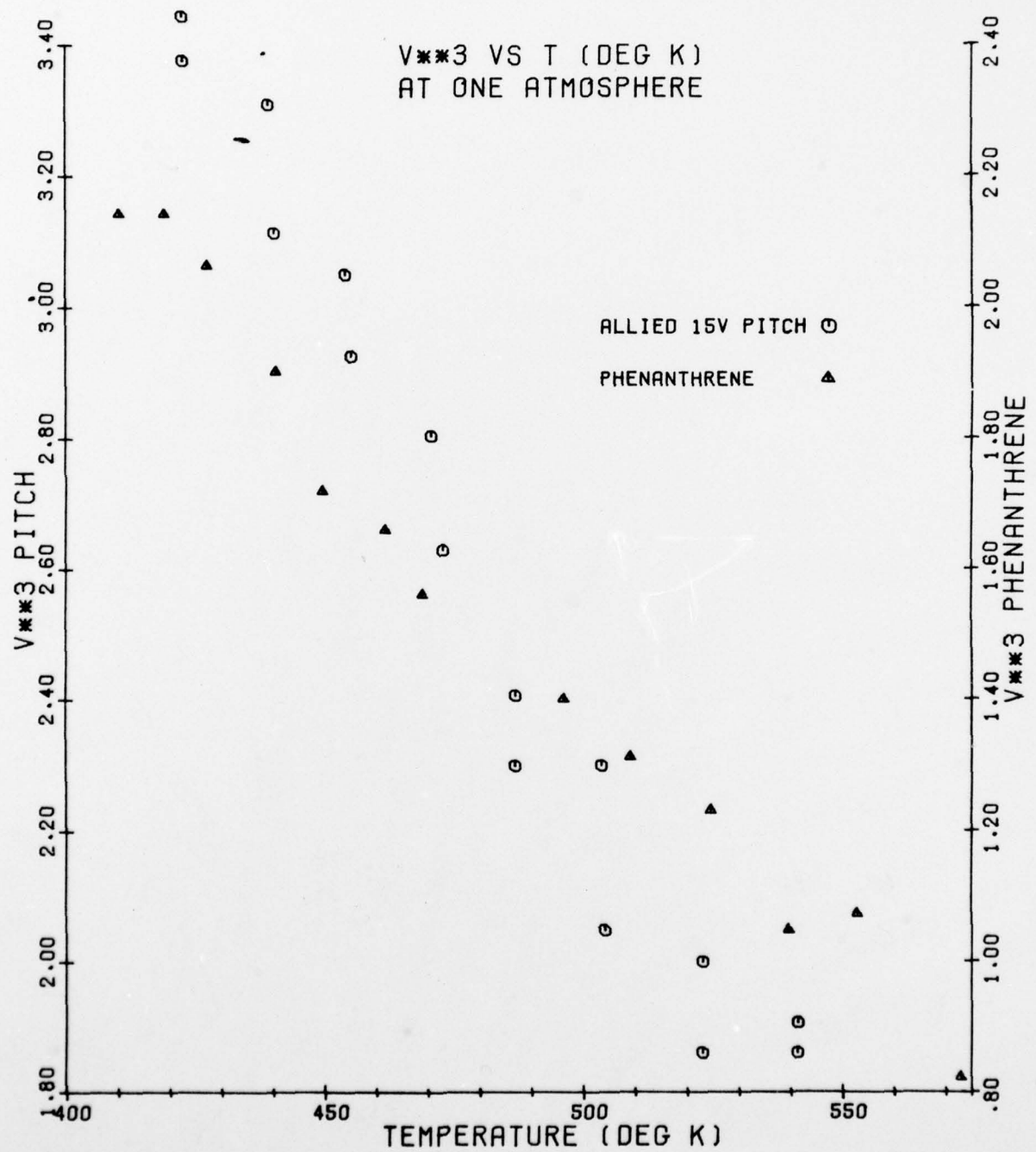
TABLE 1

SOUND VELOCITY-PRESSURE DATA
FOR WATER (30°C) AT 6 MHz

Pressure			Velocity (Km/sec)	
Kg/cm^2	MN/m^2	psig	Increasing P	Decreasing P
0	0.1	0	1.504	1.498
92	9.02	1310	1.514	1.513
307	30.1	4360	1.547	1.556
613	60.2	8730	1.600	1.606
920	90.2	13100	1.649	1.653

TABLE 2

SOUND VELOCITY IN PHENANTHRENE
AT 6.5 MHz

Temperature		Pressure MPa				
K	°C	0.1	33.77	67.53	101.3	Δ
393.5	120.5	1.333	1.332	1.334	1.336	0.006
414.7	141.7	1.287	1.289	1.291	1.293	0.006
440.2	167.2	1.234	1.236	1.237	1.239	0.005
465	192.0	1.182	1.183	1.185	1.187	0.005
491	217.8	1.129	1.131	1.133	1.134	0.005
514	241.1	1.081	1.082	1.084	1.085	0.004
538	265	1.032	1.033	1.034	1.036	0.004
562	289	0.981	0.982	0.984	--	--

TABLE 3

SOUND VELOCITY IN ALLIED 15V PITCH
AT ONE ATMOSPHERE

Temperature		Velocity (km/s)
°C	K	at 2 MHz
149	422	1.51
149	422	1.50
165	439	1.49
167	440	1.46
181	454	1.45
182	455	1.43
198	471	1.41
200	473	1.38
214	487	1.32
214	487	1.34
231	504	1.32
231	504	1.27
250	523	1.23
250	523	1.26
268	541	1.24
268	541	1.23